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**THERMODYNAMIC BEHAVIOR OF
 Ga^{3+} Al^{3+} AND Fe^{3+}
DISTRIBUTIONS IN GARNETS**

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THERMODYNAMIC BEHAVIOR OF Ga^{3+} , Al^{3+} AND Fe^{3+}
DISTRIBUTIONS IN GARNETS*

by

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August 1969

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THERMODYNAMIC BEHAVIOR OF Ga^{3+} , Al^{3+} AND Fe^{3+}

DISTRIBUTIONS IN GARNETS

ABSTRACT

Data on the distribution of Ga^{3+} , Al^{3+} and Fe^{3+} among the tetrahedral (d) and octahedral (a) sites in certain garnets were examined in terms of a thermodynamic model which yields the following expression for the distribution constant K° :

$$K^\circ = \frac{X_d (1 - X_a) \phi_{da}}{X_a (1 - X_d) \phi_{ad}}$$

Here the X 's are site occupancy fractions and the ϕ 's are equivalent to activity coefficient products. It is shown that for the elements discussed $(\phi_{da}/\phi_{ad}) \approx 1$, corresponding to ideal mixing on the individual sites. Thus we obtain

garnet	X_d, X_a	K°	$T^\circ\text{K}$
$\text{Y}_3 \text{Ga}_x \text{Fe}_{5-x} \text{O}_{12}$	$\text{Ga}^{3+}/(\text{Ga}^{3+} + \text{Fe}^{3+})$	6.71	1643
$\text{Y}_3 \text{Ga}_x \text{Al}_{5-x} \text{O}_{12}$	$\text{Ga}^{3+}/(\text{Ga}^{3+} + \text{Al}^{3+})$	~ 2.24	—
$\text{Eu}_3 \text{Ga}_x \text{Fe}_{5-x} \text{O}_{12}$	$\text{Ga}^{3+}/(\text{Ga}^{3+} + \text{Fe}^{3+})$	~ 4.46	—

where X ranges from zero to five.

With the presently available precision the calculated temperature sensitivity of K° is such that variations of several hundred degrees in the sintering temperature should be apparent.

It is stressed that this form of ideal mixing on the individual sites corresponds to nonideal mixing of the component end members $Y_3 Fe_5 O_{12}$ and $Y_3 Ga_5 O_{12}$ when referred to their mole fractions and mean molar volumes. This is consistent with the apparent positive deviation of the mean molar volume from a straight line.

THERMODYNAMIC BEHAVIOR OF Ga^{3+} , Al^{3+} AND Fe^{3+}

DISTRIBUTIONS IN GARNETS

INTRODUCTION

Nearly all crystalline materials are of a nonstoichiometric character and at the same time have atomic structures in which each atom or ion is distributed over two or more nonequivalent structural positions. In the garnets Ga^{3+} , Al^{3+} and Fe^{3+} are distributed among two different crystallographic sites with octahedral (*a*) and tetrahedral (*d*) coordinations of the O^{-2} ions. The nature of the distributions or order-disorder relations between these positions are functions of the total crystalline composition, the temperature and the pressure in the equilibrium state. In a disequilibrium state the distributions are also dependent on the previous history of the sample and on the time and provide an interesting application of chemical kinetics.

The first comprehensive treatment of the thermodynamic theory for order-disorder phenomena was provided by Bragg and Williams¹ for the simple binary alloys. Analogous treatments were subsequently given by others for the spinels. Especially noteworthy contributions were made by Néel,² Smart³ and by Callen, Harrison and Kriessman.⁴ Recently Borghese⁵ interpreted the magnetic properties of certain spinels and garnets in terms of the model in which mixing on the individual lattice sites has the character of ideal solutions. Analogous equilibrium

equations were also derived for the distribution of Mg^{2+} and Fe^{2+} among the nonequivalent structural sites of pyroxenes and amphiboles.⁶ As distinguished from the previous treatments of metallic alloys, spinels and garnets, the latter equations were formulated in terms of the atomic fractions (site occupancy fractions) of the cations on the individual sites, a procedure which will be adopted in this paper also. This formulation has the advantage of yielding more simplified data plots.

Although the effect of temperature on the intracrystalline distributions forms an important part of the problem and is implicit in all the theoretical treatments, this aspect of the problem has not been sufficiently appreciated in much of the experimental work on garnets so that more often than not the temperature of preparation of the specimens is not given. We shall attempt here to analyse the character of the solid solutions and to calculate the effect of temperature on the distribution isotherms.

OBSERVED DISTRIBUTIONS

There are three sets of experimental data for the distribution of Ga^{3+} and Fe^{3+} among the tetrahedral and octahedral sites of the garnet $\text{Y}_3\text{Ga}_x\text{Fe}_{5-x}\text{O}_{12}$, where x can in theory range from zero to five, corresponding to complete substitution of Ga^{3+} for Fe^{3+} . These data were obtained by the analysis of residual magnetic moment,⁷ nuclear magnetic resonance⁸ and by X-ray and neutron diffraction.⁹ In Fig. 1 they are plotted in terms of the atomic fraction $\text{Ga}^{3+}/(\text{Ga}^{3+} + \text{Fe}^{3+})$ (where the chemical symbols represent numbers of moles) of

gallium on the tetrahedral and octahedral sites of the total $\text{Ga}^{3+} + \text{Fe}^{3+}$ on each site.

Data for the distribution of Al^{3+} and Ga^{3+} in $\text{Y}_3 \text{Al}_x \text{Ga}_{5-x} \text{O}_{12}$ available from X-ray diffraction experiments¹⁰ are given in Table 1. Magnetic data derived from the curve of Geller et al¹¹ for $\text{Y}_3 \text{Al}_x \text{Fe}_{5-x} \text{O}_{12}$ and as discussed by Borghese⁵ are shown as points in Fig. 2 for comparison.

Table 1. Distribution of Ga^{3+} and Al^{3+} in $\text{Y}_3 \text{Ga}_x \text{Al}_{5-x} \text{O}_{12}$ and the corresponding equilibrium constant of exchange.

Data are taken from Marezio et al.¹⁰

$\text{Ga}^{3+} / (\text{Ga}^{3+} + \text{Al}^{3+})$		K°
Tetrahedral (d)	Octahedral (a)	
0.290	0.080	4.69
0.491	0.223	3.36
0.653	0.470	2.12
0.863	0.744	2.17

Some experimental points obtained for the distribution of Ga^{3+} and Fe^{3+} in the garnet $\text{Eu}_3 \text{Ga}_x \text{Fe}_{5-x} \text{O}_{12}$ by Mössbauer spectroscopy are shown in Fig. 3.

Unfortunately it is not possible to evaluate some major uncertainties in the experimental site occupancy fractions because of lack of information on the conditions of sample preparation. However according to Fischer et al⁹ the X-ray and neutron diffraction data embody probable errors of about 4 to 5 percent of

the measured values. While the scatter of points in certain parts of Fig. 1 is substantial, the overall agreement between the three sets of data is quite good.

VARIATION OF THE MEAN MOLAR VOLUME WITH COMPOSITION

The variation of the unit cell volume of $Y_3 Ga_x Fe_{5-x} O_{12}$ with $Ga^{3+}/(Ga^{3+} + Fe^{3+})$ is shown in Fig. 4. These data, which have a direct bearing on the thermodynamic interpretation of the distribution data are taken from the work of Gilleo and Geller,¹³ Espinosa,¹⁴ Euler and Brace¹⁵ and Fischer *et al.*⁹ The chief interest here is in the possible deviation from a straight line between the molar volumes of $Y_3 Ga_5 O_{12}$ and $Y_3 Fe_5 O_{12}$ since adherence of the data to such a line would be required for an ideal solid solution between these macroscopic components. Unfortunately the uncertainties in the cell volume data do not allow this question to be answered unambiguously. However, it is clear that even if a straight line were drawn through the highest volume point (that of Euler and Bruce) for $Y_3 Ga_5 O_{12}$, most of the intermediate points would still lie above this line. From the most probable straight line (drawn as dashed) this result is even clearer. If this is the true picture, it is clear that there is a positive excess molar volume and that the garnet solid solutions as a whole is non-ideal in character.

THERMODYNAMIC CHARACTER OF THE SOLID SOLUTIONS

If the dependence on composition of the free energy of exchange between the nonequivalent lattice sites is largely confined to the entropy of mixing terms, it is convenient to write¹⁶ the following expression for a quasibinary crystal such as a garnet:

$$K^{\circ} = \frac{X_d (1 - X_a) \phi_{da}}{X_a (1 - X_d) \phi_{ad}} \quad (1)$$

Here the X 's are the site occupancy fractions of one of the two exchangeable species on the octahedral (a) and tetrahedral (d) sites, K° is the equilibrium constant and the ϕ factors are analogous to activity coefficient products and are derived from kinetic formulae. By definition K° is a function only of the temperature and the pressure (or volume) while the ϕ 's are also functions of the total composition. However, only the temperature dependency is significant for these condensed systems at low to intermediate pressures.

The site occupancy fractions are related to the total mole fraction X_t of a given end member (such as $Y_3 Ga_5 O_{12}$) as

$$X_t = \frac{3}{5} X_d + \frac{2}{5} X_a \quad (2)$$

The simplest and most convenient form of equation (1) is one for which (ϕ_{da}/ϕ_{ad}) = 1 and in which all compositional dependency is confined to the entropy of mixing on the individual a and d sites. This then is a form of "ideal" solution, which is however sharply differentiated for the ideal solution for the crystal as a whole and for which the activity a_t of a component end member (such as $Y_3 Ga_5 O_{12}$) is set equal to X_t . Rather this activity (normalized to $1/5 Y_3 Ga_5 O_{12}$) is

$$a_t = X_d^{3/5} X_a^{2/5} \quad (3)$$

Obviously (2) and (3) can be equal only if $X_d = X_a$ when $K^\circ = 1$. However in the model under discussion $K^\circ \neq 1$ even at the highest temperatures except as a limiting case since, unlike the nonequivalent sites in metallic alloys, the tetrahedral and octahedral sites always retain their identities.

The curve of Fig. 1 is a fit of equation (1) to the observed data for $Y_3 Ga_x Fe_{5-x} O_{12}$. In this case X_d and X_a refer to the atomic fraction $Ga^{3+}/(Ga^{3+} + Fe^{3+})$ on the tetrahedral and octahedral sites respectively. Except for some local scatter the data are quite well represented by the curve corresponding to $K^\circ = K_1^\circ = 6.71$.

Fig. 2 shows the analogous curve as derived from equation (1) with X_d and X_a equal to the atomic fraction $Al^{3+}/(Al^{3+} + Fe^{3+})$ on the tetrahedral and octahedral sites of $Y_3 Al_x Fe_{5-x} O_{12}$. This curve corresponds to an equilibrium constant $K^\circ = K_2^\circ = 3$ as derived by Borghese.⁵ Borghese has shown that his version of equation (1) combined with his formula for the magnetic moment yields a better representation of the magnetic data than do the plotted points in Fig. 2. In fact it may be shown that the curve from which the latter are derived is inconsistent with the thermodynamic model and equation (1) in any form. We therefore accept the value $K_2^\circ = 3$ as derived by Borghese.

The data of figures 1 and 2 should be directly related to those of Marezio et al as given in Table 1 if certain simplifying assumptions are introduced, for we have the following related exchange reactions and equilibrium constants:



in which a and d refer to the octahedral and tetrahedral sites. If we now assume that the mixing properties of the ions are invariant with respect to which other ion is present we obtain

$$\frac{K_1^\circ}{K_2^\circ} = K_3^\circ = 2.24$$

Table 1 shows the values of K° as derived from the data of Marezio et al.¹⁰

Although the correspondence with $K_3^\circ = 2.24$ is quite good for several specimens the others differ considerably from this value. It is not known if these differences are attributable to the uncertainties in the data such as arise from the conditions of sintering or to a failure of the assumptions employed in the model.

The distribution curve and the corresponding equilibrium constant K_4° for the distribution of Ga^{3+} and Fe^{3+} among the tetrahedral and octahedral sites of $\text{Eu}_3 \text{Ga}_x \text{Fe}_{5-x} \text{O}_{12}$ are shown in Fig. 3. In this case the curve gives a quite good fit with $K_4^\circ = 4.46$ if the most Ga-rich sample is disregarded. It is clear

from a comparison of these data with Fig. 1 that the substitution of europium for yttrium tends to favor Fe^{3+} in the tetrahedral site. However here again it must be remembered that the effect of the thermal history is unknown.

Taken together, figures 1 and 4 point up an interesting feature of the thermodynamics. If the data of Fig. 1 truly correspond to the simplified model with $(\phi_{da}/\phi_{ad}) = 1$ the system is a form of ideal solution in which the only compositional dependence of the free energy comes from the entropy of mixing on the individual sites as given by equation (3). However this result in turn implies non-ideal mixing between the macroscopic components $\text{Y}_3\text{Ga}_5\text{O}_{12}$ and $\text{Y}_3\text{Fe}_5\text{O}_{12}$ in which the sites are not distinguished. The apparent positive deviation from a straight line of the mean molar volume in Fig. 4 is compatible with this interpretation.

EFFECT OF TEMPERATURE

Of primary interest is the determination of the effect of temperatures of annealing on the equilibrium constants. This effect could of course be evaluated directly if ΔH° the standard enthalpy of exchange were known, since

$$\frac{\partial \ln K^\circ}{\partial T} = \frac{\Delta H^\circ}{RT^2} .$$

However, in the absence of independent knowledge of ΔH° we can estimate ΔG° , the Gibbs free energy of exchange from the distribution data of Fig. 1 for which the annealing temperature is known, since

$$\Delta G^\circ = - RT \ln K^\circ \quad (4)$$

According to Fischer et al⁹ the temperature of sintering for their specimens was 1643°K and since $K_1^\circ = 6.71$ we obtain $\Delta G_1^\circ = - 6220$ calories. Also we have the general relation

$$\frac{\partial \Delta G_1^\circ}{\partial T} = - \Delta S_1^\circ ,$$

where ΔS° is the standard entropy of exchange.

Now we have reason to suspect that ΔS_1° will be small since the system is condensed and no large volume changes are involved. Also, this anticipation has recently been substantiated for the case of the order-disorder relations of Fe^{2+} and Mg^{2+} in $(Mg, Fe) SiO_3$ (orthopyroxene),¹⁶ which represents a situation closely parallel to the garnets.

Thus if $\Delta S_1^\circ \simeq 0$ we have

$$\Delta H_1^\circ \simeq \Delta G_1^\circ .$$

and the temperature effect can be estimated directly for equation (4). This has been done for five isotherms in Fig. 5.

If Fig. 5 is valid indication of the temperature sensitivity of K_1° , it is clear that from the amount of scatter shown in Fig. 1 variations of several hundred degrees in sintering temperatures should be detectable. It is unfortunate that the thermal histories of most of the specimens are unknown.

Equation (2) and the isotherms of Fig. 5 can also be used to estimate deviations from ideal mixing on the individual sites from systematic deviations of the data from the isotherms. The excess free energy contributions for such a source should have the same effect proportionally as temperature variations. It is possible that some of the deviations from the data points from the isotherm of Fig. 1 are attributable to this source, but the uncertainties in the data preclude any quantitative estimate of the effect at this time.

EQUATION OF THE EXCHANGE KINETICS

Although no kinetic data exist for the exchange reactions in garnets, it is interesting to write down the phenomenological form of the rate equations. This may be done if we assume as did Dienes¹⁸ that the rate controlling process is the exchange rather than some other process such as nucleation. Thus if C_0 is the concentration (in moles or particles per cm^3) of the total tetrahedrally and octahedrally coordinated ions we obtain the following equation¹⁶ for the rate of change of concentration of one of the ions on the tetrahedral site:

$$\begin{aligned}
 -\frac{dX_d}{dt} &= \frac{2}{5} C_0 K_{da} \phi_{da} X_d (1 - X_a) \\
 &\quad - \frac{2}{5} C_0 K_{ad} \phi_{ad} X_a (1 - X_d) .
 \end{aligned} \tag{5}$$

This is related to rate of change on the other site as

$$\frac{3}{2} \frac{dX_a}{dt} = - \frac{dX_d}{dt} .$$

K_{ad} and K_{da} are the specific rate constants for exchange in the two directions. It is apparent that when $(dX_d/dt) = 0$ equation (5) reduces to equation (1). The important point to be made here is that although ϕ_{da}/ϕ_{ad} may approach unity with essentially ideal mixing on the stable lattice sites, the individual ϕ 's may deviate widely from unity. The reason for this is that these factors embody the thermodynamic properties of the transitional state and mixing in this state might be far from ideal. Of course, if mixing were also ideal in the transitional state the ϕ 's would reduce to unity and equation (5) would assume its simplest form.

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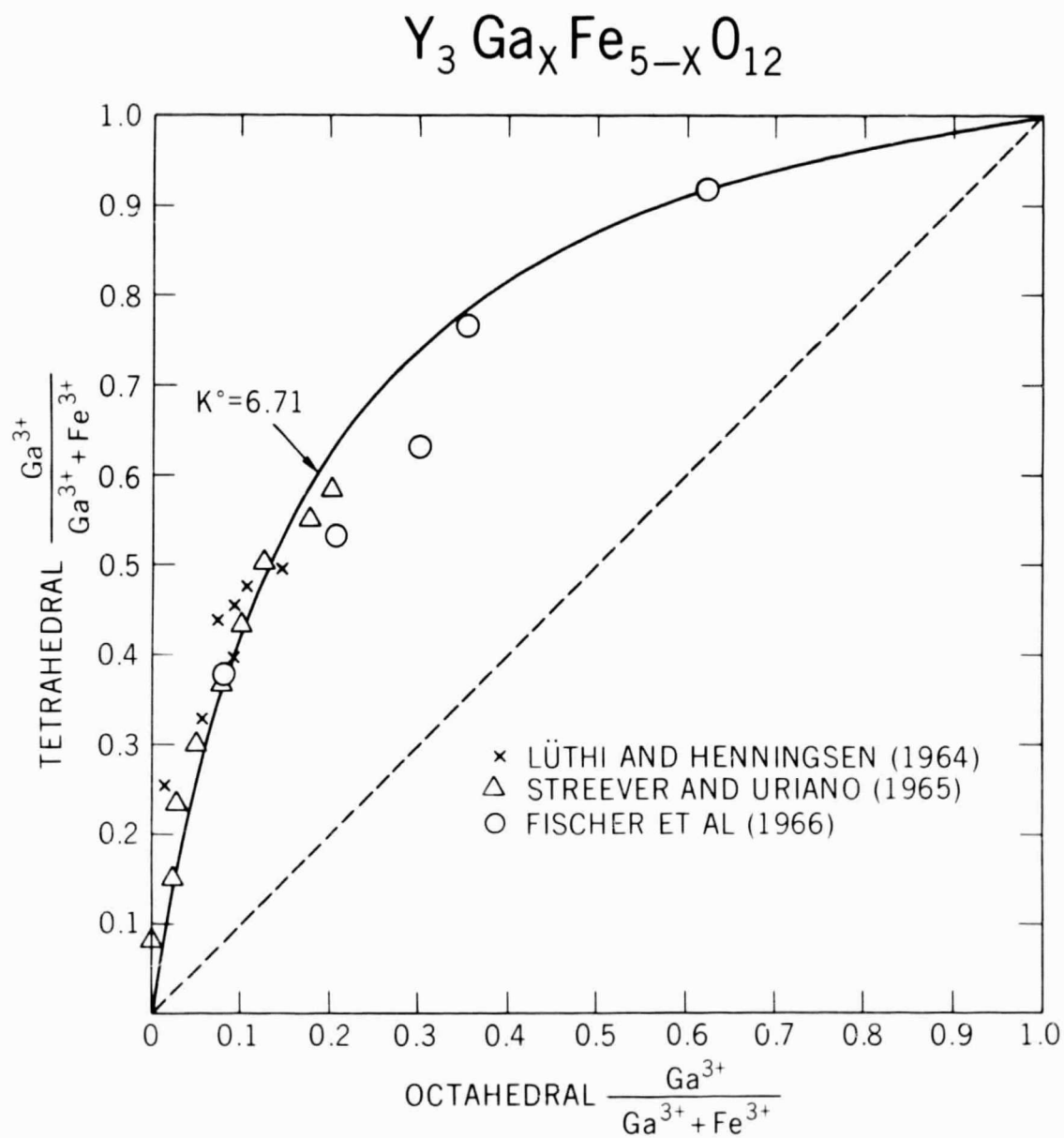


Figure 1—Distribution of Ga^{3+} and Fe^{3+} among the tetrahedral and octahedral sites of $Y_3 Ga_x Fe_{5-x} O_{12}$. The equilibrium constant K° is also shown.

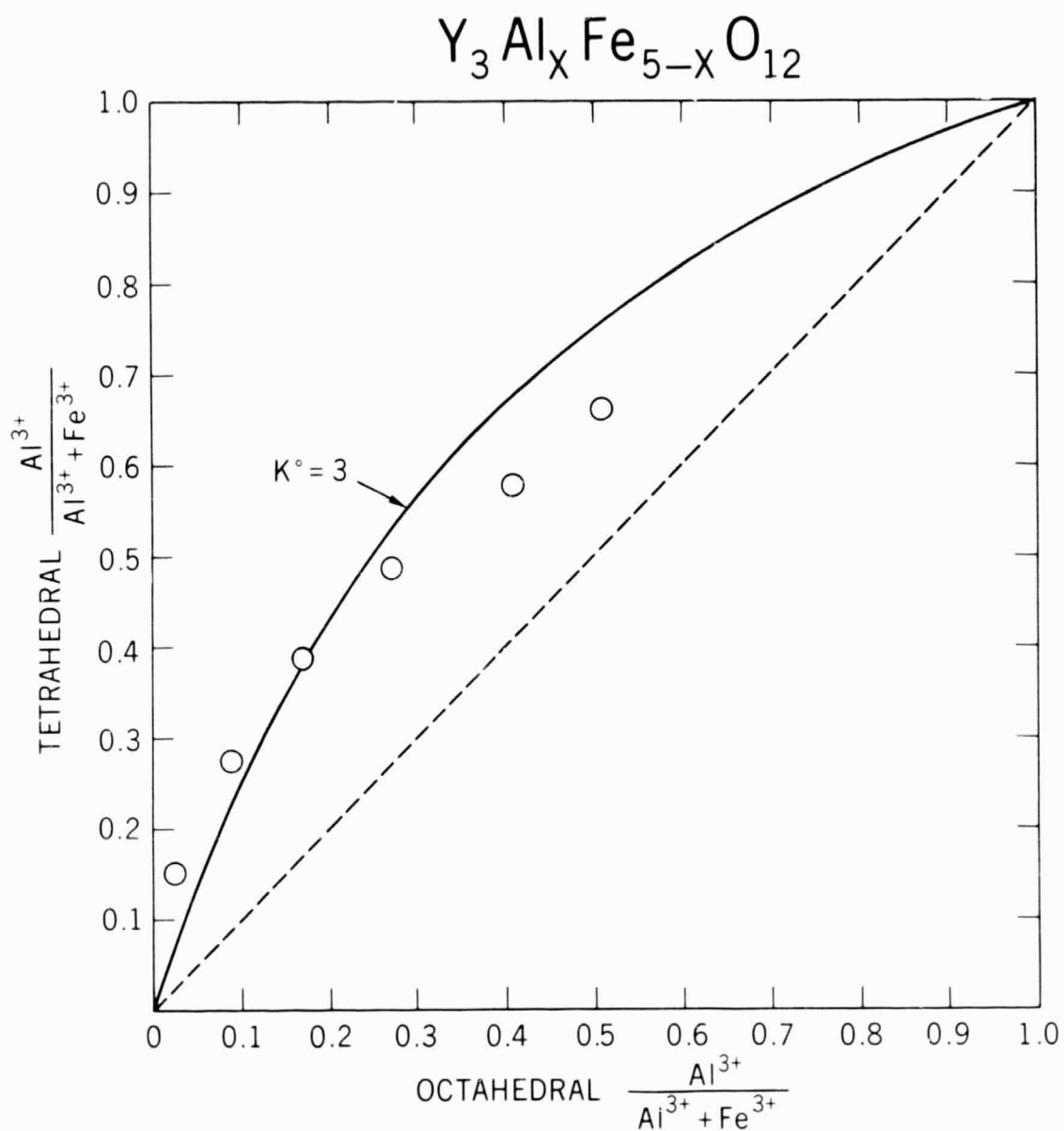


Figure 2—Distribution of Al^{3+} and Fe^{3+} among the tetrahedral and octahedral sites of $Y_3 Al_x Fe_{5-x} O_{12}$. The points are derived from the curve of Geller *et al*¹¹ and the curve and equilibrium constant are from Borghese.⁵

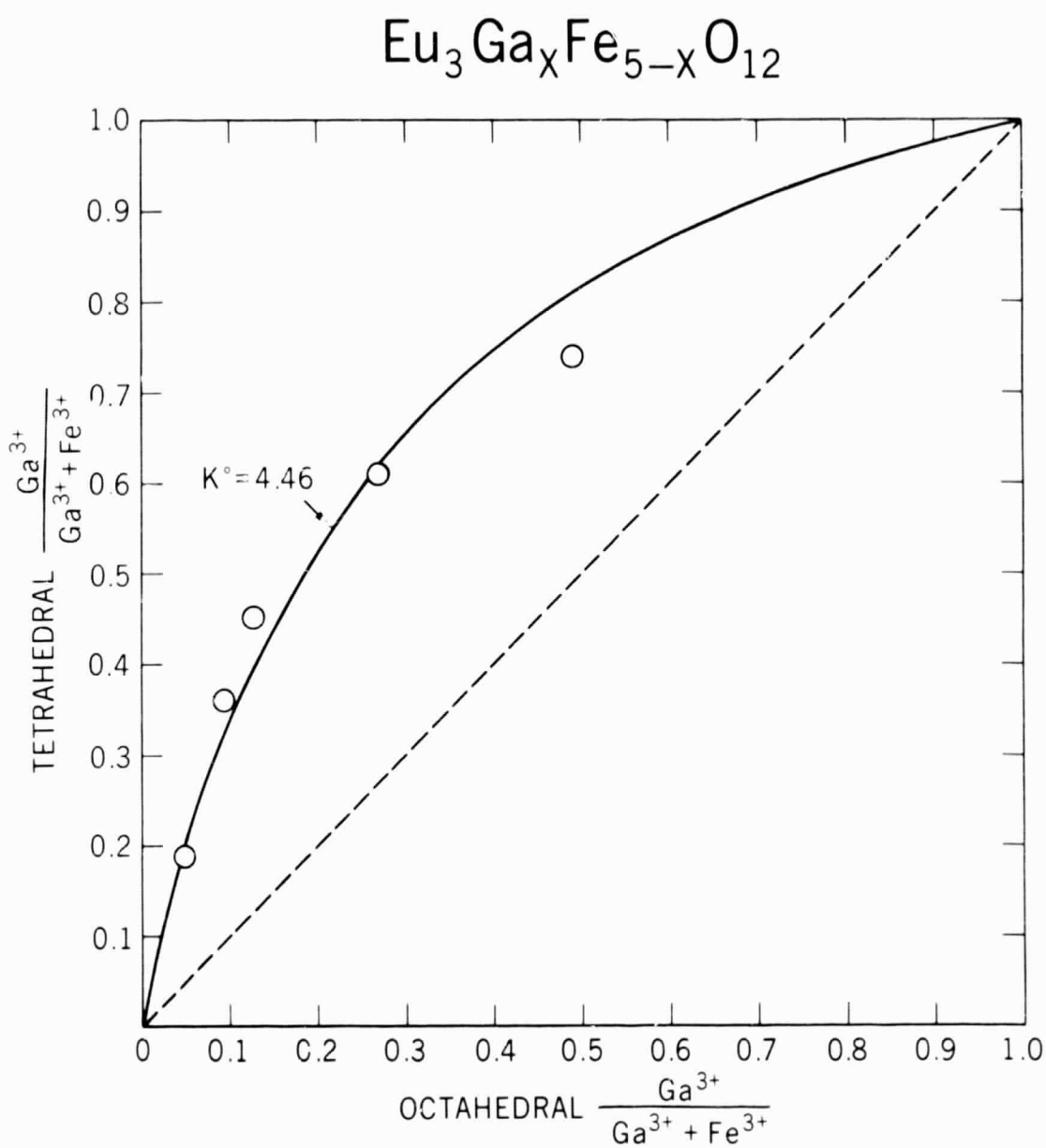


Figure 3—Distribution of Ga^{3+} and Fe^{3+} among the tetrahedral and octahedral sites of $\text{Eu}_3\text{Ga}_x\text{Fe}_{5-x}\text{O}_{12}$. Data points are derived from the work of Nowik and Ofer.¹²

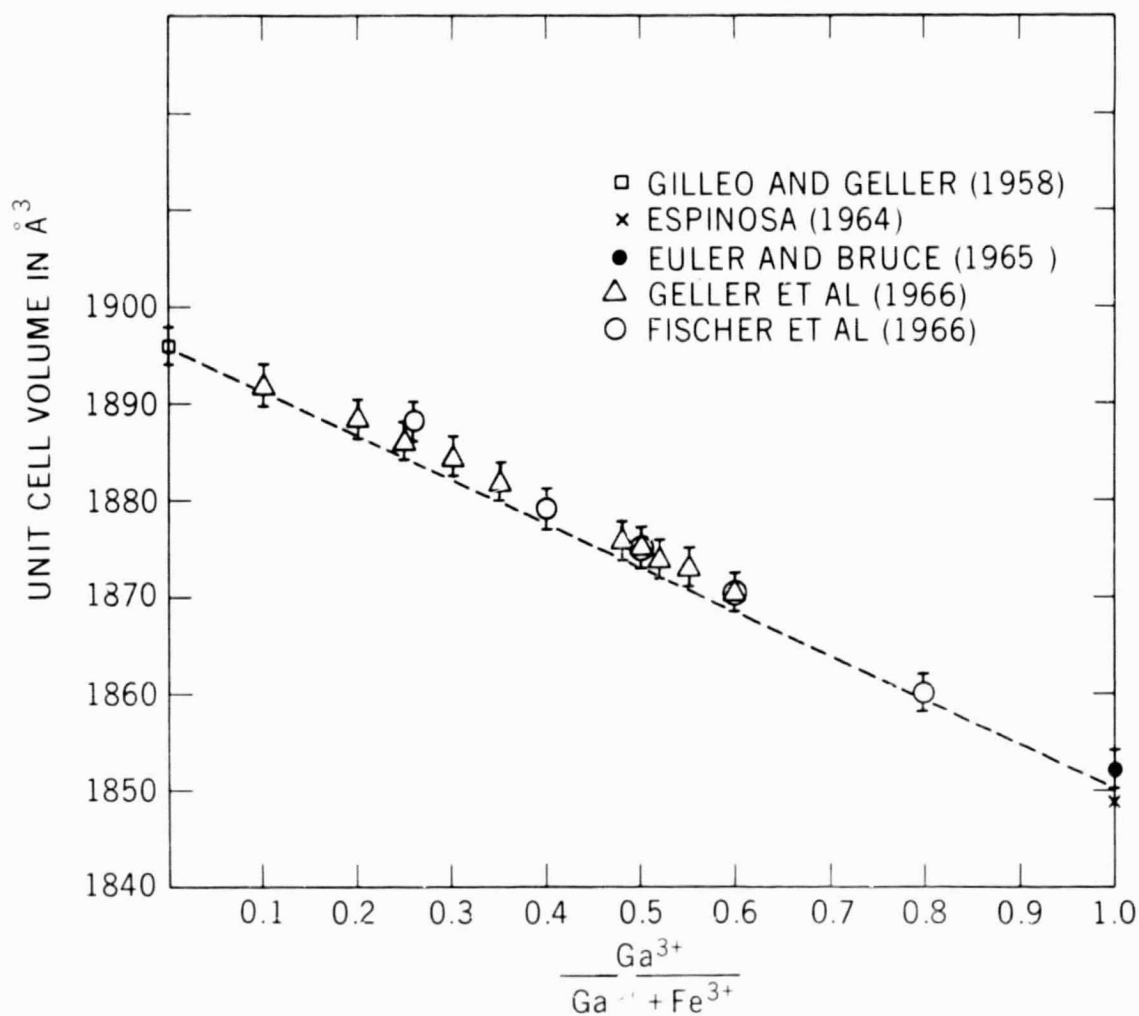
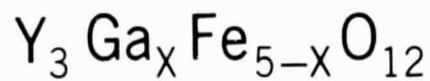


Figure 4—Cell volumes (in Å³) as a function of composition in $\text{Y}_3 \text{Ga}_x \text{Fe}_{5-x} \text{O}_{12}$.
The cell volumes are directly proportional to the mean molar volumes.

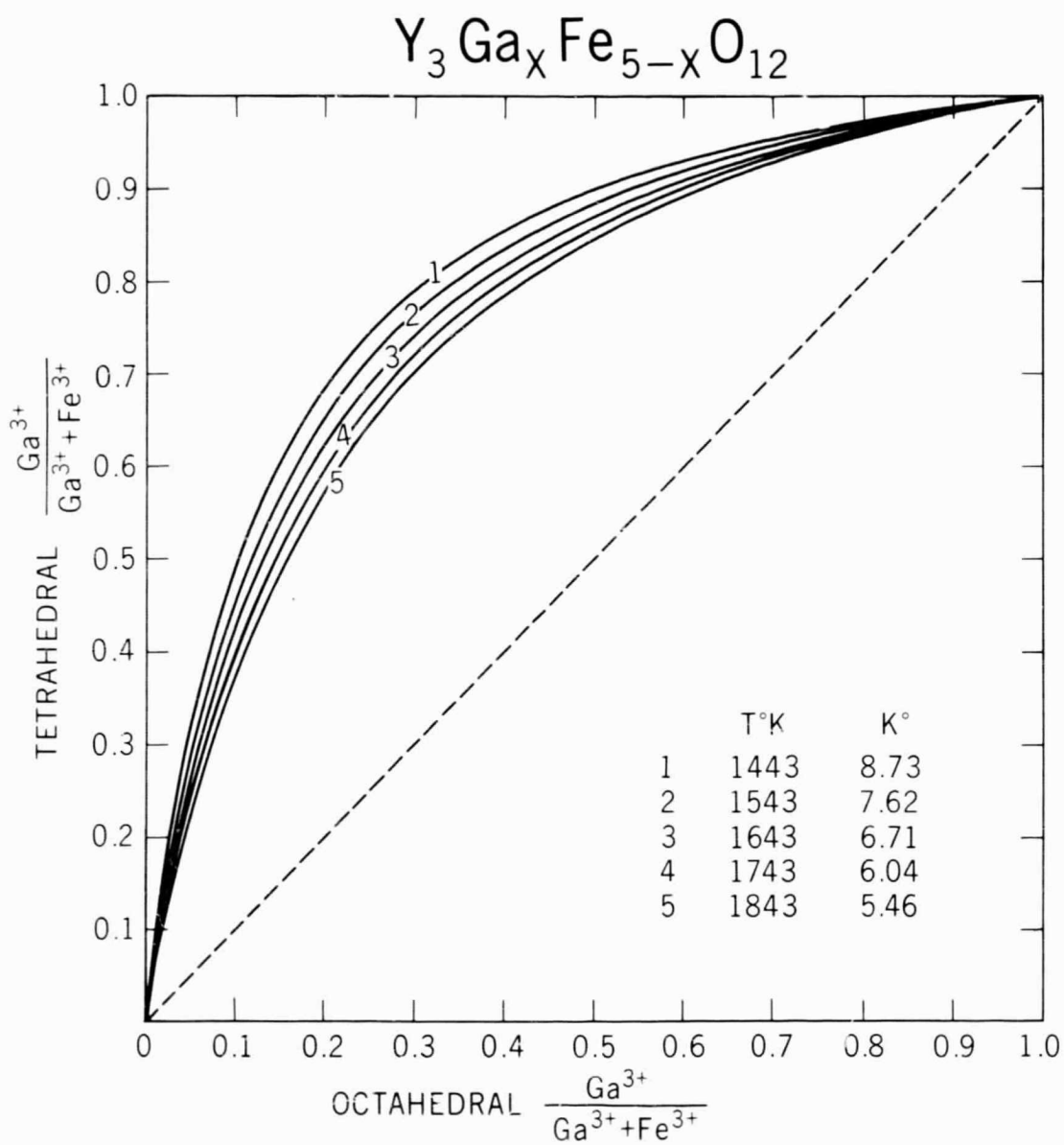


Figure 5—Calculated isotherms for different temperatures from the model which assumes ideal mixing on the individual sites of $Y_3 Ga_x Fe_{5-x} O_{12}$.